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THE EFFECT OF Au NANOCCLUSERS IN TIN OXIDE FILM GAS SENSORS

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Abstract: The effect of Au nanoparticles in SnO₂ was investigated for gas sensor applications. The films were prepared by the sol–gel method. HAuCl₄ was added to a tin alkoxide solution, the mixture was hydrolyzed and spin coated on glass substrates. The samples were then thermally treated to remove the organics. The films were characterized by thermogravimetric analysis, scanning electron microscopy, and X-ray diffraction. Additionally, the optical absorbance and the reflectivity were measured. The films were tested against hydrogen. The change of the electrical conductivity was used to detect the gas. The response of SnO₂ and SnO₂–Au to H₂ was investigated at different temperatures and concentrations. With the addition of Au nanoparticles the detection limit decreased, the working temperature was reduced (from 180°C to 140°C), and there was a ten times increase of the signal.

Keywords: SnO₂ thin films; Au nanoparticles; hydrogen sensor

1. Introduction

Gas sensors based on metal oxide sensitive layers are playing an important role in the detection of toxic pollutants and inflammable gases. Metal oxides and especially tin dioxide is widely used as a basic material for the preparation of gas sensing devices operating in these applications.^{1–3} The effect of

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the addition of many different metallic particles on the gas sensing properties of metal oxides has been widely studied, but the results depend on the experimental conditions and the method of fabrication.⁴

Hydrogen is an abundant, renewable, efficient, clean energy source. As an industrial gas, it is currently used in a large number of areas, e.g. chemistry (crude oil refining, plastics, as a reducing environment in float glass industry, etc.), food products (hydrogenation of oils and fats), semiconductors (as a processing gas in thin film deposition and annealing atmospheres), and transportation (as fuel in fuel cells and space vehicle rockets).

All these applications require the development of hydrogen sensing devices that allow safe control of the gas usage. Devices capable of detecting the presence of hydrogen above the low explosion limit (LEL) of 40,000 ppm have become indispensable to prevent explosions.⁵

A pure alkoxide method has been used to prepare SnO₂ thin films undoped and doped with Au nanoparticles. The films prepared were tested as H₂ sensors.

2. Experimental

The substrates (glass slides) were cleaned by soaking for 24 h in a sulfurochromic bath and kept in isopropanol until used. A HAuCl₄ solution in ethanol was prepared by dissolving Au in HNO₃/3HCl, then dried under vacuum; the remaining yellow crystals of HAuCl₄ were dissolved in ethanol to obtain a 0.3M solution. The tin alkoxide starting solution was obtained from pure SnCl₄ using the NH₃ gas method. The working solution was prepared by mixing the tin alkoxide starting solution with the HAuCl₄ solution. The solution obtained was aged by stirring at room temperature for 24 h. After spinning, the tin oxide gel films were dried at R.T. for 24 h and then heat-treated for 2 h at 510°C in air. The thickness of the films was approximately 90 nm, as measured by means of an alpha step apparatus.

The films were characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Additionally, the optical absorbance and the reflectivity were measured.

Hydrogen sensing tests were performed in an aluminum vacuum chamber. The chamber was evacuated down to 1 Pa, then filled with dry air at atmospheric pressure. The SnO₂ and Au–SnO₂ thin films were tested in the temperature range of 147–180°C at hydrogen concentrations from 10,000 to 500 ppm. The hydrogen concentration was calculated on the basis on the partial pressures of the sensing gas and air inside the chamber. A bias of 1 V was applied, and the current through the film was measured with a Keithley Mo. 485 Picoammeter. Current modifications helped to monitor the hydrogen sensing.

3. Results and Discussion

Thermogravimetric analysis showed that the isopropanol and the water evaporate at 118°C while the remaining organics are burned up to 400°C. At 400°C the HAuCl_4 is reduced to metallic Au. Over 500°C there is no loss of mass (Figure 1a). In the XRD diagram a clear tendency of texturing in the [101] crystalline direction of the tetragonal rutile structure can be seen (Figure 1b). A homogeneous dispersion of irregularly shaped Au nanoparticles with dimensions of few hundreds nanometers is observed in the SEM image (Figure 2a). The surface plasmon resonance (SPR) is the peak at 560 nm in the absorption spectrum (Figure 2b). According to the FWHM, the size of the Au nanoparticles is 3.5 nm.

Figure 1. TGA (left) and XRD diagram (right) of a SnO_2 -Au film.

Figure 2. SEM image (left) and UV-VIS spectrum (right) of a SnO_2 -Au film.

The response of SnO_2 and SnO_2 -Au to H_2 was investigated at different temperatures and concentrations. SnO_2 films did not respond at all at temperatures lower than 180°C. With the addition of Au nanoparticles, the detection limit decreased, the working temperature was reduced (from 180°C to 140°C), and there was a ten times increase of the signal (Figure 3).

Figure 3. Response of Au-SnO₂ and SnO₂ thin films at 147°C and 181°C, respectively.

4. Conclusions

The doping of SnO₂ with Au nanoparticles decreased the sensor working temperature with respect to the undoped one by 40°C, while the response increased by more than ten times.

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